Tin−Copper Transmetalation: Cross-Coupling of α-Heteroatom-Substituted Alkyltributylstannanes with Organohalides

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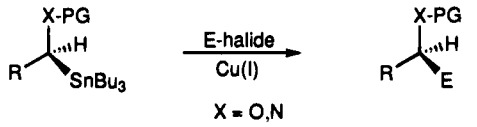
Abstract: Copper(I), in the absence of other transition metals, catalyzes the cross-coupling of (α-(acyloxy)benzyl)-tributylstannanes with allylic bromides in THF in fair to good yields and with aryl/vinyl halides less efficiently or not at all. Simple (α-(acyloxy)alkyl)tributylstannanes react sluggishly even with allyl bromide. However, proximal thiosubstituents on either reaction partner dramatically enhance yields, reaction rates, and the variety of suitable educts. (α-Phthalimidoylalkyl)tributylstannanes afford protected α-amino thio esters. In contrast with the Stille reaction, copper-mediated cross-couplings of α-heteroatom-substituted alkyltributylstannanes proceed with complete retention of configuration via a coordinatively stabilized organocopper intermediate that can be intercepted in good yield by 1,4-conjugate addition to 2-cyclohexen-1-one.

Introduction

The palladium-catalyzed cross-coupling of tetraorganostannanes with organic electrophiles, known as the Stille reaction, has emerged as one of the premier methods for the creation of new carbon−carbon bonds.[1] Its scope, functional group compatibility, and stereospecificity are often complementary to those of more conventional anionic processes based on stannyl transmetalation.[2] In 1990, Liebeskind *et al.*[3] introduced the use of cocatalytic copper for lethargic or otherwise refractory Stille reactions and this modification has been extensively utilized for transferring sp^2 carbon centers from tin.[4] More recently, Piers and Wong[5] achieved efficient intramolecular unions between vinyltrialkylstannanes and vinyl halides under the influence of stoichiometric amounts (2−3 equiv) of CuCl in DMF. The generality of their observation, however, is not known, and its application to the transfer of sp^3 carbons has not been explored.

In our laboratory and that of others,[6] the utility of Pd/Cu cocatalysis was extended to Stille-type substitutions between (α-(acyloxyalkyl)/(phthalimidoalkyl)tributylstannanes and acyl chlorides to give α-heteroatom-substituted ketones in moderate to good yields. Notably, these couplings displayed complete retention of configuration at the tin-bearing carbon and the reaction was subsequently exploited in an efficient asymmetric total synthesis of the anticancer C-glycoside (+)-goniofufurone by cross-coupling a glycosylstannane with benzoyl chloride.[7]

We now report that *catalytic amounts* of copper salts, without Pd,[8] are capable of mediating the cross-coupling of α-heteroatom-substituted alkyltributylstannanes with a variety of organic halides and that proximal thio substituents[9] can have a profound influence (eq 1). Additionally, evidence is presented to support the hypothesis[10] that a tin−copper transmetalation occurs under the reaction conditions.



(1)

PG = Ac, Bz, MOM, $Ph_2P(O)$, Phthalimide, PhOC(S), RR'NC(S), MeC(S)

E = Allyl, Propargyl, Phenyl, Benzoyl, Acyl, PhOC(S), EtSC(O)

Results and Discussion

An initial survey of representative organic electrophiles demonstrated that catalytic copper salts, in the absence of other transition metals, significantly facilitate their cross-coupling with α-heteroatom-substituted alkyltributylstannanes (Table 1). Best results were obtained in nonpolar, organic solvents using CuCN,[11] nominally at 8 mol %. The actual concentration of catalyst in solution was clearly much less since the majority of the salt does not dissolve. In fact, heating a suspension of CuCN in anhydrous THF for 8 h, cooling to 45 °C, and filtration afforded a homogeneous solution that analyzed for $\sim 5 \times 10^{-8}$ M copper. This solution was comparable in catalytic activity to the original CuCN suspension. There was, however, no cross-

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1995.

(1) Reviews: (a) Mitchell, T. N. *Synthesis* **1992**, 803−815. (b) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworth: Boston, MA, 1987.

(2) (a) Behling, J. R.; Babiak, K. A.; Ng, J. S.; Campbell, A. L.; Moretti, R.; Koerner, M.; Lipshutz, B. H. *J. Am. Chem. Soc.* **1988**, *110*, 2641−2643. (b) Still, W. C.; Sreekumar, C. *Ibid.* **1980**, *102*, 1201−1202. (c) Linderman, R. J.; Griedel, B. D. *J. Org. Chem.* **1991**, *56*, 5491−5493. (d) McGarvey, G. J.; Kimura, M. *Ibid.* **1985**, *50*, 4655−4657.

(3) Liebeskind, L. S.; Foster, B. S. *J. Am. Chem. Soc.* **1990**, *112*, 8612−8613. Liebeskind, L. S.; Fengl, R. W. *J. Org. Chem.* **1990**, *55*, 5359−5364.

(4) Malm, J.; Bjork, P.; Gronowitz, S.; Hörnfeldt, A.-B. *Tetrahedron Lett.* **1994**, *35*, 3195−3196. Satoh, T.; Kokubo, K.; Miura, M.; Nomura, M. *Organometallics* **1994**, *13*, 4431−4436. Saa, J. M.; Martorell, G. *J. Org. Chem.* **1993**, *58*, 1963−1966. Liebeskind, L. S.; Riesinger, S. W. *Ibid.* **1993**, *58*, 408−413. Gomez-Bengoa, E.; Echavarren, A. M. *Ibid.* **1991**, *56*, 3497−3501. Palmisano, G.; Santagostino, M. *Tetrahedron* **1993**, *49*, 2533−2542. Ichikawa, J.; Ikeura, C.; Minami, T. *Synlett* **1992**, 739−740.

(5) Piers, E.; Wong, T. *J. Org. Chem.* **1993**, *58*, 3609−3610.

(6) (a) Ye, J.; Bhatt, R. K.; Falck, J. R. *J. Am. Chem. Soc.* **1994**, *116*, 1−5. Also see: (b) Linderman, R. J.; Graves, D. M.; Kwochka, W. R.; Ghannam, A. F.; Anklekar, T. V. *Ibid.* **1990**, *112*, 7438− 7439.

(7) Ye, J.; Bhatt, R. K.; Falck, J. R. *Tetrahedron Lett.* **1993**, *34*, 8007−8010.

(8) All glassware, magnetic stirring bars, syringes, etc., were fresh from the manufacturer and were never in contact with transition metals prior to their use in this study.

(9) The participation of coordinating or chelating heteroatom substituents in organometallic additions and stabilization has ample precedent: Hanessian, S.; Thavonekham, B.; DeHoff, B. *J. Org. Chem.* **1989**, *54*, 5831−5833 and cited references. Hoveyda, A. H.; Evans, D. A.; Fu, G. C. *Chem. Rev.* **1993**, *93*, 1307−1370.

(10) Farina, V.; Kapadia, S.; Krishnan, B.; Wang, C.; Liebeskind, L. S. *J. Org. Chem.* **1994**, *59*, 5905−5911.

(11) Other catalysts also gave coupled products, e.g., CuI, $Cu[O_2C(CH_2)_{16}CH_3]_2$, $(Ph_3P)_3RhCl$, and $CuCl_2$, but in lower yields. Lewis acids (e.g., $BF_3{\cdot}Et_2O$) were partially effective when thio substituents were present.

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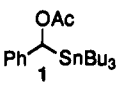
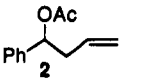
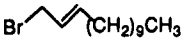
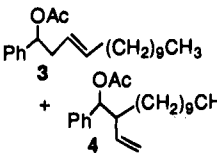
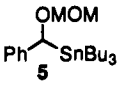
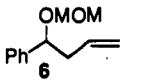
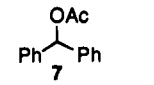
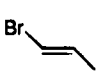
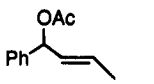
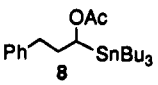
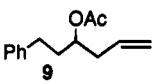
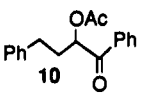
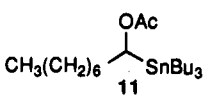
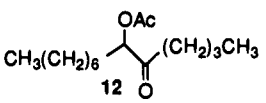
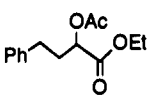
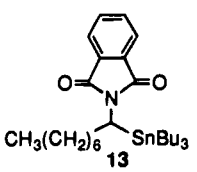
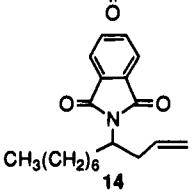
Table 1. Cu(I)-Catalyzed Coupling of α-Substituted Stannanes with Electrophiles[a]

Entry	Stannane	Electrophile	Solvent/Temp (°C)/Time (h)	Adduct	Yield (%)
a	 1		THF, 65, 27	 2	80
b	1		THF, 55, 21	 3 + 4	76 (7:3)
c	 5		PhCH$_3$, 100, 24	 6	45
d	1	I-Ph	THF, 60, 48	 7	50
e	1	Br-Ph	PhCH$_3$, 110, 50	7	20[b]
f	1		THF, 60, 48		0
g	 8		THF, 65, 18	 9	15
h	8		PhCH$_3$, 80, 20	 10	22
i	 11		PhH, 60, 6	 12	<10
j	8		PhCH$_3$, 100, 44		0
k	 13		THF, 65, 44	 14	50

[a] Catalyzed by 8 mol % CuCN. [b] Ca. 40% of the stanyl starting material was recovered.

coupling in the absence of copper. At odds with our experience[6a] in cross-coupling acid chlorides, cocatalysis by Cu(I) and Pd(0) usually did not enhance the yields and in some cases was detrimental to the reactions in Table 1.[12]

The migratory aptitude for coupling generally followed the hierarchy previously observed,[6a] with α-oxygenated benzylstannanes being the most reactive. This was, however, strongly influenced by the nature of the substitution on the heteroatom. For instance, (α-(acetyloxy)benzyl)tributylstannane (**1**) reacted smoothly with allyl bromide and a homolog to give good yields of the homoallylic adducts **2** and **3**/**4**, respectively (Table 1, entries a and b). Competing S_N2/S_N2' attack[13] explains the presence of regioisomers **3**/**4** in the latter example, since control experiments revealed no isomerization of the precursors or products under the reaction conditions. Comparable cross-couplings with propargylic halides also generated mixtures (~3:1) of the expected substitution products and allenes. α-Oxygenated stannanes modified with ether substituents (e.g., methyl), in contrast, were sluggish substrates. Only poor to modest yields of adduct could be teased from these reactions and then only in the case of MOM (entry c) or related ethers capable of chelation.[6a] Among halides bonded to sp^2 carbons, aryl iodides (e.g., entry d) normally gave preparatively useful results with **1**, while aryl bromides (entry e) required forcing conditions and vinyl bromides (entry f) failed completely.

Simple (α-(acyloxy)alkyl)stannanes proved lackluster as a group under these circumstances. Even when paired with relatively puissant electrophiles like allyl bromide (entry g), acid chlorides (entries h and i), and ethyl chloroformate (entry j), the outcomes were disappointing. Yet, (α-phthalimidooctyl)tributylstannane (**14**) was an unexpectedly good substrate by comparison (entry k).

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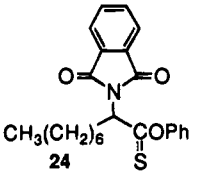
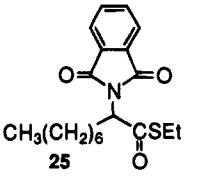
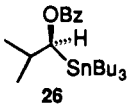
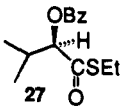
The foregoing results seemed most consistent with an obligatory tin to copper transmetalation prior to coupling. If this were the case, then strategically placed coordinating groups[9] could stabilize the nascent copper intermediate and possibly

(12) See ref 19 for an exception.

(13) Similar ratios of S_N2/S_N2' products are obtained using conventionally prepared organocopper reagents: Lipshutz, B. H.; Sengupta, S. *Org. React.* **1982**, *41*, 135–631.

Table 2. Cu(I)-Catalyzed Coupling of α-Substituted Stannanes with Thiochloroformates[a]

Entry	Stannane	Thioformate	Temp (°C)/Time (h)	Adduct	Yield (%)
a	**1**	Cl-C(=S)COPh	75, 15	Ph(OAc)CH-C(=S)COPh **15**	96
b	**1**	Cl-C(=O)CSEt	75, 21	Ph(OAc)CH-C(=O)CSEt **16**	98
c	**5**	Cl-C(=S)COPh	85, 36	Ph(OMOM)CH-C(=S)COPh **17**	83
d	**8**	Cl-C(=S)COPh	80, 17	Ph-CH2-CH(OAc)-C(=S)COPh **18**	98
e	**8**	Cl-C(=O)CSEt	80, 35	Ph-CH2-CH(OAc)-C(=O)CSEt **19**	97
f	*tert*-Bu-CH(OAc)-SnBu3 **20**	Cl-C(=S)COPh	80, 54	*tert*-Bu-CH(OAc)-C(=S)COPh **21**	70
g	CH3-CH2-CH=CH-CH(OBz)-SnBu3 **22**	Cl-C(=S)COPh	70, 17	CH3-CH2-CH=CH-CH(OBz)-C(=S)COPh **23**	65
h	**13**	Cl-C(=S)COPh	75, 70	 **24**	92
i	**13**	Cl-C(=O)CSEt	75, 70	 **25**	85
j	 **26**	Cl-C(=O)CSEt	80, 68	 **27**	73

[a] Ca. 1 M solution in toluene with 8 mol % CuCN.

improve the synthetic outcome. The consequences of this expectation are summarized in Table 2.[14] Additions of (α-(acetyloxy)benzyl)tributylstannane (**1**) to thiono (Table 2, entry a) and thiol (entry b) chloroformates in toluene gave outstanding results. The α-acetyloxy thio ester adducts **15** and **16** were readily identified by their distinctive ^{13}C NMR and infrared signatures.[15] Even the nature of the protecting group on the α-oxygen substituent was not noticeably important (entry c) when using thiochloroformates. The usually more subdued (α-(acetyloxy)alkyl)stannane **8** (entries d and e) was also well behaved (cf. Table 1, entry j) as was the sterically crowded neopentyl version **20** (entry f). Reaction of the allylic (1-(benzoyloxy)-2-hexenyl)tributylstannane (**22**) gave rise to only modest amounts of cross-coupled adduct **23** (entry g) accompanied by several unidentified, minor byproducts. This may reflect the proclivity of the starting material toward rearrangement, especially under the influence of Lewis acids.[16] As observed above, α-phthalimidoyl stannane **13**[17] was relatively reactive and, thus, provided convenient access to some otherwise difficult to prepare thio analogs of α-amino acids (entries h and i).

Surprisingly, dry air had scant effect on the preceding reactions, although the solvent was clearly an important factor. Under otherwise identical conditions, the yield of thiono ester **18** (Table 2, entry d) progressively decreased to 73%, 45%, and 8% when toluene was replaced with THF, dioxane, and 1,2-dichloroethane, respectively. On the other hand, sulfur containing additives, *inter alia*, thiourea, thio esters, elemental sulfur, potassium ethyl xanthate, and 2-mercaptopyridine (so-

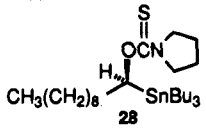
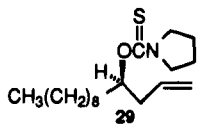
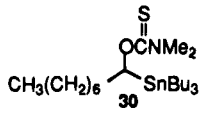
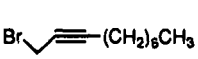
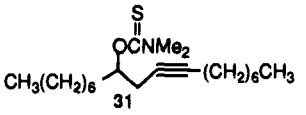
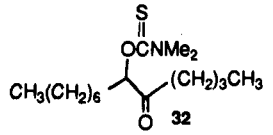
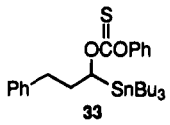
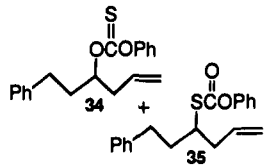
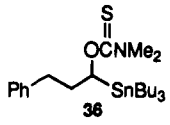
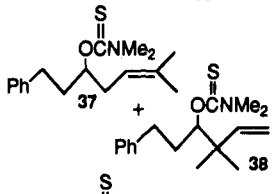
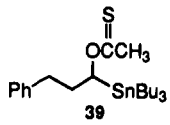
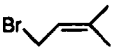
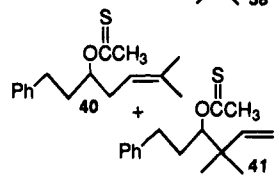
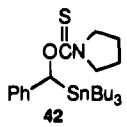
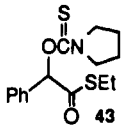
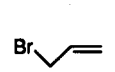
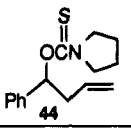
(14) Similar cross-couplings with α-(acyloxy) tributylstannanes prepared from ketones were not successful. For instance, heating 1-(acetyloxy)-1-(tributylstannyl)cyclohexane with phenyl chlorothionoformate in the presence of 8 mol % CuCN in toluene at 55–60 °C led to decomposition of the starting materials.

(15) Lemarie, M.; Pham, T.-N.; Metzner, P. *Tetrahedron Lett.* **1991**, *32*, 7411–7414.

(16) Marshall, J. A.; Gung, W.-Y. *Tetrahedron Lett.* **1989**, *30*, 2183–2186.

(17) *N*-Benzoyl and *N*-carbobenzoxy derivatives of primary and secondary α-amino stannanes gave poor results.

Table 3. Cu(I)-Catalyzed Cross-Coupling of α-Thiono-Substituted Stannanes[a]

Entry	Stannane	E-halide	Solv/Temp/Time (h)	Adduct	yield (%)
a	 **28**		THF, 45, 12	 **29**	95
b	 **30**		PhH, 45, 11	 **31**	84[b]
c	**30**		PhH, 60, 6	 **32**	82
d	 **33**		THF, 45, 25	 **34** + **35**	71 (1 : 2)
e	 **36**		THF, 23, 10	 **37** + **38**	92[c] (1.2 : 1)
f	 **39**		THF, 23, 8	 **40** + **41**	78[d] (3.5 : 1)
g	 **42**		THF, 50, 16	 **43**	77
h	**42**		THF, 23, 9	 **44**	99

[a] Catalyzed by 8 mol % CuCN. [b] 5-6% of the corresponding allene was also isolated. [c] Minor amounts (2−3%) of thiono to thiol rearrangement products were also isolated. [d] Thiono to thiol rearrangement products (9%) were isolated.

dium salt) were generally innocuous, although some of the examples in Table 1 did show improvement with CS_2 as a cosolvent.

To gain additional insight into the mechanism of the copper-mediated cross-couplings in Table 2, (*S*)-(1-(benzoyloxy)-2-methylpropyl)tributylstannane (**26**) (84% ee) was prepared by sequential BINAL-H asymmetric reduction[18] of the corresponding acylstannane and benzoylation. Coupling under the standard conditions using CuCN led to *S*-ethyl (*R*)-2-(benzoyloxy)-3-methylthiobutyrate (**27**) (Table 2, entry j) in 73% yield.[19] Chiral HPLC analysis using an independently synthesized standard confirmed carbon−carbon bond formation proceeded with ca. 98% retention of configuration. This is what would be expected from an initial Sn/Cu transmetalation[2] and contrasts with Pd-catalyzed Stille reactions of tetraalkylstannanes where complete inversion of configuration at the α-stannyl center has been demonstrated.[20] Farina and Liebeskind have recently provided spectroscopic data for the existence of such an organocopper intermediate as part of a "dual mechanism" responsible for the "copper effect" in Stille reactions.[10] However, mechanistic conclusions concerning cross-couplings of α-heteroatom-substituted stannanes should be approached cautiously since both Pd-catalyzed and Pd/Cu-cocatalyzed reactions result in retention of configuration.[6a] Consequently, more direct evidence for the involvement of an organocopper intermediate in Cu-catalyzed couplings of α-heteroatom-substituted stannanes would be desirable (*vide infra*).

Placing the thio substituent adjacent to the α-stannyl center had the most dramatic effect of any modification. Couplings were comparatively milder, faster, and more productive (Table 3). Exposure of (α-(carbamoyloxy)alkyl)stannanes **28** and **30** to allyl bromide (entry a), a propargylic bromide (entry b), and an aliphatic acid chloride (entry c), combinations that previously gave poor results (cf. Table 1, entries g and i), afforded excellent yields of coupled products. As above, substitution at the

(18) Chan, P. C.-M.; Chong, J. M. *J. Org. Chem.* **1988**, *53*, 5586−5588.

(19) Contrary to the usual lack of effect by cocatalytic Pd, coupling mediated by a combination of 8 mol % each CuCN and $PdCl_2$ (dppf) gave the *S*-ethyl thio ester in 70% yield with retention of configuration but, in this instance, required only 25 h at 68 °C.

(20) Labadie, J. W.; Stille, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 6129−6137.

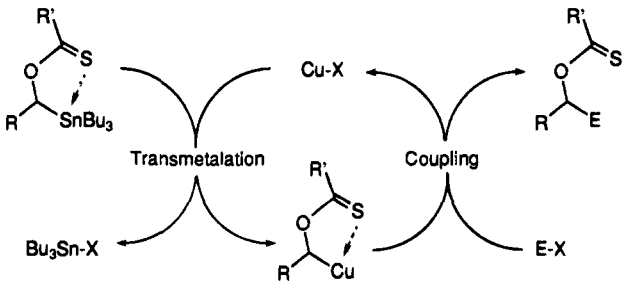


Figure 1. Catalytic cycle.

stannyl-bearing carbon was totally stereospecific (entry a). The α-thionocarbonate derivative **33** furnished lower but still acceptable yields of C−C products (entry d). However, the rapid thiono/thiol rearrangement,[21] i.e., **34** to **35**, limits this group's synthetic utility. With prenyl bromide, regioisomeric addition proved troublesome but could be controlled to some degree by the choice of the coordinating group on the α-heteroatom, e.g., thionocarbamoyl **36** (entry e) vs thiono ester **39** (entry f), among other parameters.[13]

Cross-couplings of the benzylic thionocarbamate **42**, as anticipated, were quite facile (entries g and h). However, even **42** could not be coaxed into reacting with aryl triflates or allyl acetate. Nevertheless, other aspects of its behavior are worth noting. For instance, the union of **42** with allyl bromide (entry h) could be duplicated (92% yield), in the absence of any catalyst including copper,[8] by simply warming both components together at 45 °C for 21 h. The mechanism of this transformation is obscure at present;[22] however, inclusion of 8 mol % of Et_3N or 1,2-bis(diphenylphosphino)ethane blocked all coupling and the starting materials could be recovered.

Comparisons of the ^1H, ^{13}C, and ^{119}Sn spectra of α-acetyloxy stannanes **1** and **8** with their α-thionocarbamoyloxy counterparts **42** and **36** revealed only minor chemical shift differences and did not support the notion that rehybridization at tin induced by complexation with sulfur (as depicted in **45**) was a viable explanation for their vastly different reactivities. Instead, we favor the formation of a coordinatively stabilized organocopper intermediate as part of an efficient catalytic cycle (Figure 1). The coordinating heteroatom appears to have an optimum range of softness[23] (or hardness) and a preferred geometry for complexation. For instance, the thiocarbonates **46** and **47** along with sulfide **48** failed to react with allyl bromide under conditions where the related thionocarbonate **33** (Table 3, entry d) and thiono ester **39** (entry f) gave satisfactory results. At higher temperatures, **46**−**48** decomposed. Conversely, cross-coupling of 2-thiophene **49** and diphenylphosphinate **51** with allyl bromide led to **50** and **52** in 50% and 66% yields, respectively. Importantly, moving the coordinating group to a site somewhat remote from the reaction center, as in **53**, abolished its influence and no C−C bond formation was observed.

In initial studies, we have been able to intercept the putative organocopper intermediate by heating **54** with CuCN (8 mol %) in DME at 50 °C in the presence of 2-cyclohexen-1-one and excess TMSCl for 7 h.[24] The resultant Michael conjugate **55** was isolated in 79% yield as a 2:1 diastereomeric mixture, after hydrolytic workup. More detailed investigations into the scope and potential applications of this chemistry are in progress and will be reported in due course.

Experimental Section

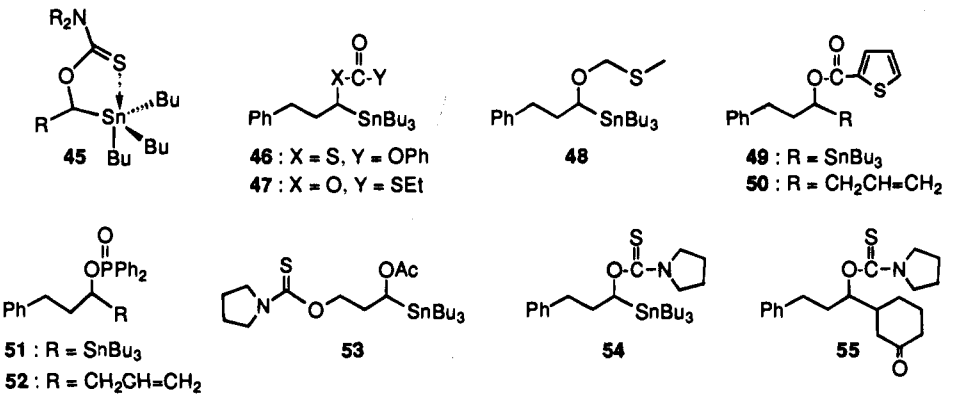
Reagents and Procedures. Chromatography, elemental analyses, and routine laboratory manipulations were as previously reported.[25] Optical purities were measured by analyzing the NMR spectrum of the corresponding Mosher ester[26] or by chiral phase HPLC. ^{119}Sn spectra were recorded on a Varian VXR-500 using tetramethylstannane as the internal reference. Transition metal trace analyses were performed by Galbraith Laboratories (Knoxville, TN). All reactions were maintained under an argon atmosphere unless otherwise noted. Compounds **1**, **5**, **11**, **13**, and **20** were prepared as previously described.[6a,27] The protected α-heteroatom-substituted stannanes could be stored for several months without significant degradation when maintained at ≤20 °C and under an inert atmosphere; brief exposure of the stannanes to the atmosphere during weighing and handling appeared to have no adverse effect. All organic electrophiles were from commercial sources and were used as received.

Copper-Catalyzed Coupling (General Procedure). To a solution of α-heteroatom-substituted stannane (1.1 mmol) and CuCN (8 mol %) in anhydrous solvent (5 mL) was added the organic electrophile (1.0 mmol). The reaction mixture was maintained in a sealed tube under argon for the time and at the temperature indicated in Tables 1−3. The CuCN usually remained as a suspension. Removal of all volatiles *in vacuo* and chromatography of the residue on silica gel afforded the adducts in the indicated yields (Tables 1−3).

1-(Acetyloxy)-1-phenyl-3-butene (2). Cross-coupling of **1** with allyl bromide as described in the general procedure gave the title adduct as a colorless oil (80%): TLC (SiO_2) EtOAc/hexane (1:9), $R_f \sim 0.39$; ^1H NMR δ 7.25−7.40 (m, 5H), 5.80 (dd, J = 5.9, 13.7 Hz, 1H), 5.58−5.79 (m, 1H), 5.00−5.12 (m, 2H), 2.50−2.67 (m, 2H), 2.07 (s, 3H); ^{13}C NMR: δ 170.22, 140.07, 133.31, 128.40, 127.93, 126.54, 117.99, 75.12, 40.73, 21.19; MS (CI, CH_4) *m/z* (relative intensity) 189 [(M − H)$^+$, 0.5], 169 (4), 149 (62), 107 (100). A sample was solvolyzed using 5% NaOMe/MeOH for 6 h to give 1-phenyl-3-buten-1-ol identical by TLC and ^1H NMR with an authentic sample.[29]

1-(Acetyloxy)-1-phenyltetradec-3-ene (3)/3-(α-(Acetyloxy)benzyl)-tridec-1-ene (4). Cross-coupling of **1** with 1-bromo-2-tridecene as described in the general procedure gave the title adducts as an inseparable 7:3 mixture (76%): TLC (SiO_2) EtOAc/hexane (1:9), $R_f \sim 0.44$; ^1H NMR δ 7.20−7.40 (m, 5H), 4.85−5.80 (m, 3H), 2.30−2.64 (m, 2H), 2.02 (s, 3H), 1.82−2.00 (m, 2H), 1.05−1.40 (m, 16H), 0.92 (br t, J = 6.3 Hz, 3H); ^{13}C NMR δ 170.68, 138.45, 137.63, 128.34, 128.20, 117.35, 78.40, 49.22, 39.64, 32.55, 31.92, 29.63, 29.36, 27.02, 22.69, 21.25, 14.13; HRMS (EI) calcd for $C_{22}H_{34}O_2$ *m/z* 330.2559, found *m/z* 330.2565.

1-(Methoxymethoxy)-1-phenyl-3-butene (6). Cross-coupling of **5** with allyl bromide as described in the general procedure gave the title adduct as a colorless oil (45%): TLC (SiO_2) EtOAc/hexane (1:9), R_f



~ 0.41; ^{1}H NMR δ 7.28−7.40 (m, 5H), 5.80 (ddt, J = 3.9, 7.9, 14.2 Hz, 1H), 5.04−5.16 (m, 2H), 4.62 (dd, J = 5.7, 7.9 Hz, 1H), 4.54 (s, 2H), 3.48 (s, 3H), 2.40−2.59 (m, 2H); ^{13}C NMR δ 134.77, 128.34, 127.67, 126.92, 117.14, 94.08, 79.38, 55.71, 42.80. A sample was solvolyzed using 5% methanolic HCl for 6 h to give 1-phenyl-3-buten-1-ol identical by TLC and ^{1}H NMR with an authentic sample.[29]

***O*-Acetylbenzhydrol (7).** Cross-coupling of **1** with bromo- or iodobenzene as described in the general procedure gave the title adduct as a colorless oil in 20 and 50% yields, respectively. TLC (SiO_2) EtOAc/hexane (3:7), R_f ~ 0.49. TLC and ^{1}H/^{13}C NMR spectra were identical with an authentic sample.

(1-(Acetyloxy)-3-phenylpropyl)tributylstannane (8). The title compound was obtained[6a] from dihydrocinnamaldehyde and Ac_2O as a colorless oil (73%) after chromatography using EtOAc/hexane (5:95): ^{1}H NMR δ 7.12−7.30 (m, 5H), 4.75 (dd, J = 5.4, 7.6 Hz, 1H), 2.55−2.75 (m, 2H), 1.90−2.25 (m, 2H), 2.00 (s, 3H), 1.40−1.55 (m, 6H), 1.22−1.39 (m, 6H), 0.90−1.00 (m, 15H); ^{13}C NMR δ 171.27, 141.68, 128.37, 128.30, 125.81, 71.13, 36.00, 34.18, 28.98, 27.40, 13.65, 9.54; MS (CI, CH_4) m/z (relative intensity) 468 (M^+, 0.5), 411 (93), 409 (98), 353 (24), 277 (31), 247 (27), 177 (31), 84 (82), 51 (100); HRMS (EI) calcd for $C_{19}H_{31}O_2Sn$ ($M - C_4H_9$)$^+$ m/z 411.1348, found m/z 411.1354.

1-Phenyl-3-(acetyloxy)-5-hexene (9). Cross-coupling of **8** with allyl bromide as described in the general procedure gave the title adduct as a colorless oil (15%): TLC (SiO_2) EtOAc/hexane (1:4), R_f ~ 0.63; ^{1}H NMR δ 7.15−7.35 (m, 5H), 5.62−5.80 (m, 1H), 5.01−5.13 (m, 2H), 4.95−5.00 (m, 1H), 2.58−2.68 (m, 2H), 2.55 (t, J = 7.2 Hz, 2H), 2.08 (s, 3H), 1.83−1.98 (m, 2H); ^{13}C NMR δ 170.76, 141.50, 133.48, 128.41, 128.31, 125.93, 117.84, 72.85, 38.69, 35.26, 31.76, 21.20; HRMS (EI) calcd for $C_{14}H_{18}O_2$ m/z 218.1307, found m/z 218.1310.

1-(Acetyloxy)-3-phenylpropyl Phenyl Ketone (10). Cross-coupling of **8** with benzoyl chloride as described in the general procedure gave the title adduct as a colorless oil (22%): TLC (SiO_2) EtOAc/hexane (1:4), R_f ~ 0.30; ^{1}H NMR δ 7.78−7.81 (m, 2H), 7.50−7.60 (m, 1H), 7.30−7.43 (m, 2H), 7.18−7.28 (m, 3H), 7.10−7.18 (m, 2H), 5.81 (t, J = 6.4 Hz, 1H), 2.62−2.71 (m, 2H), 2.19 (s, 3H), 2.08−2.19 (m, 2H); ^{13}C NMR δ 196.31, 167.63, 140.32, 130.55, 128.75, 128.60, 128.48, 128.36, 126.35, 74.39, 32.89, 31.80, 20.66, 10.69; HRMS (EI) calcd for $C_{18}H_{18}O_3$ m/z 282.1256, found m/z 282.1258.

6-(Acetyloxy)tridec-5-one (12). Cross-coupling of **11** with pentanoyl chloride as described in the general procedure gave the title adduct as a colorless oil (8−10%): TLC (SiO_2) EtOAc/hexane (3:17), R_f ~ 0.33; ^{1}H NMR δ 5.00 (dd, J = 4.7, 7.9 Hz, 1H), 2.33−2.52 (m, 2H), 2.19 (s, 3H), 1.12−1.78 (m, 16H), 0.83−1.00 (m, 6H); HRMS (EI) calcd for $C_{15}H_{28}O_3$ m/z 256.2038, found m/z 256.2040.

4-Phthalimidoundec-1-ene (14). Cross-coupling of **13** with allyl bromide as described in the general procedure gave the title adduct as a colorless oil (50%): TLC (SiO_2) 15% EtOAc/hexane, R_f ~ 0.60; ^{1}H NMR δ 0.82 (t, J = 6.5 Hz, 3H), 1.05−1.40 (m, 10H), 1.62−1.81 (m, 1H), 2.01−2.20 (m, 1H), 2.43−2.58 (m, 1H), 2.68−2.88 (m, 1H), 4.22−4.32 (m, 1H), 4.90−5.05 (m, 1H), 5.62− 5.80 (m, 1H), 7.66−7.70 (m, 2H), 7.76−7.82 (m, 2H); ^{13}C NMR δ 14.05, 22.59, 26.67, 29.13, 29.16, 31.74, 32.07, 37.03, 51.77, 117.63, 123.08, 131.80, 133.79, 134.79, 168.71; HRMS (EI) calcd for $C_{19}H_{25}NO_2$ m/z 299.1885, found m/z 299.1883.

***O*-Phenyl 2-(Acetyloxy)-2-phenylthioacetate (15).** Cross-coupling of **1** with phenyl chlorothionoformate as described in the general procedure gave the title adduct as a colorless oil (96%): TLC (SiO_2) EtOAc/hexane (1:9), R_f ~ 0.30; ^{1}H NMR δ 7.63−7.70 (m, 2H), 7.23−7.50 (m, 6H), 6.90−6.98 (m, 2H), 6.42 (s, 1H), 2.21 (s, 3H); ^{13}C NMR δ 215.55, 170.15, 153.84, 135.33, 129.57, 129.22, 128.77, 127.55, 126.61, 121.49, 81.21, 21.11; HRMS (EI) calcd for $C_{16}H_{14}O_3S$ m/z 286.0664, found m/z 286.0653.

***S*-Ethyl 2-(Acetyloxy)-2-phenylthioacetate (16).** Cross-coupling of **1** with ethyl chlorothiolformate as described in the general procedure gave the title adduct as a colorless oil (98%): TLC (SiO_2) EtOAc/hexane (1:9), R_f ~ 0.29; ^{1}H NMR δ 7.41−7.52 (m, 2H), 7.30−7.40 (m, 3H), 6.12 (s, 1H), 2.88 (q, J = 7.4 Hz, 2H), 2.21 (s, 3H), 1.22 (t, J = 7.4 Hz, 3H); ^{13}C NMR δ 197.01, 169.66, 134.30, 129.22, 128.77, 127.61, 80.02, 23.14, 20.84, 14.25; HRMS (EI) calcd for $C_{12}H_{14}O_3S$ m/z 238.0664, found m/z 238.0662.

Phenyl *O*-(Methoxymethyl)thionomandelate (17). Cross-coupling of **5** with phenyl chlorothionoformate as described in the general procedure gave the title adduct as a colorless oil (83%): TLC (SiO_2) EtOAc/hexane (1:9), R_f ~ 0.27; ^{1}H NMR δ 7.60−7.71 (m, 2H), 7.30−7.50 (m, 5H), 7.15−7.22 (m, 1H), 6.84−6.91 (m, 2H), 5.66 (s, 1H), 4.90 (d, J = 6.9 Hz, 1H), 4.80 (d, J = 6.9 Hz, 1H), 3.42 (s, 3H); ^{13}C NMR δ 218.62, 154.05, 137.49, 129.56, 128.69, 128.62, 127.23, 126.49, 121.49, 95.06, 84.26, 56.11; HRMS (EI) calcd for $C_{16}H_{16}O_3S$ m/z 288.0820, found m/z 288.0822.

***O*-Phenyl 2-(Acetyloxy)-4-phenylthiobutryate (18).** Cross-coupling of **8** with phenyl chlorothionoformate as described in the general procedure gave the title adduct as a colorless oil (98%): TLC (SiO_2) EtOAc/hexane (1:9), R_f ~ 0.30; ^{1}H NMR δ 7.36−7.44 (m, 2H), 7.18−7.35 (m, 6H), 6.92−7.04 (m, 2H), 5.41 (dd, J = 5.1, 7.7 Hz, 1H), 2.80−2.94 (m, 2H), 2.28−2.41 (m, 2H), 2.18 (s, 3H); ^{13}C NMR δ 217.81, 170.39, 153.56, 140.48, 129.65, 128.58, 128.43, 126.64, 126.28, 121.60, 79.20, 35.67, 31.56, 20.96; HRMS (EI) calcd for $C_{18}H_{18}O_3S$ m/z 314.0977, found m/z 314.0981.

***S*-Ethyl 2-(Acetyloxy)-4-phenylthiobutyrate (19).** Cross-coupling of **8** with ethyl chlorothiolformate as described in the general procedure gave the title adduct as a colorless oil (97%): TLC (SiO_2) EtOAc/hexane (1:9), R_f ~ 0.29; ^{1}H NMR δ 7.21−7.40 (m, 5H), 5.24 (dd, J = 5.0, 7.7 Hz, 1H), 2.98 (q, J = 7.5 Hz, 2H), 2.78 (t, J = 7.2 Hz, 2H), 2.22 (s, 3H), 2.12−2.24 (m, 2H), 1.28 (t, J = 7.5 Hz, 3H); ^{13}C NMR δ 199.02, 170.07, 140.40, 128.58, 128.43, 126.28, 77.81, 33.65, 31.15, 22.80, 20.75, 14.41; HRMS (EI) calcd for $C_{14}H_{18}O_3S$ m/z 266.0977, found m/z 266.0970.

***O*-Phenyl 2-(Acetyloxy)-3,3-dimethylthiobutyrate (21).** Cross-coupling of **20** with phenyl chlorothionoformate as described in the general procedure gave the title adduct as a colorless oil (70%): TLC (SiO_2) EtOAc/hexane (1:9), R_f ~ 0.41; ^{1}H NMR δ 7.38−7.45 (m, 2H), 7.25−7.34 (m, 1H), 6.98−7.10 (m, 2H), 5.19 (s, 1H), 2.19 (s, 3H), 1.19 (s, 9H); ^{13}C NMR δ 216.33, 170.68, 153.94, 129.65, 126.55, 121.76, 86.66, 34.88, 26.58, 20.99; HRMS (EI) calcd for $C_{14}H_{18}O_3S$ m/z 266.0977, found m/z 266.0972.

(1-(Benzyloxy)hex-2-enyl)tributylstannane (22). The title compound was obtained[6a] from *trans*-2-hexenal and benzoyl chloride as a colorless oil (53%) after chromatography using EtOAc/hexane (5:95): ^{1}H NMR δ 8.00−8.10 (m, 2H), 7.41−7.60 (m, 3H), 5.71−5.82 (m, 1H), 5.41−5.60 (m, 2H), 1.94−2.03 (m, 2H), 1.20−1.56 (m, 14H), 0.82−0.98 (m, 18H); ^{13}C NMR δ 166.32, 132.59, 130.71, 129.52, 129.42, 128.29, 125.98, 72.36, 34.38, 28.98, 27.40, 22.87, 13.77, 13.67, 10.01; MS (CI, CH_4) m/z (relative intensity) 436 [($M - C_4H_9$)$^+$, 7], 355 (77), 353 (58), 291 (29), 241 (11), 177 (8), 105 (100); HRMS (EI) calcd for $C_{21}H_{33}O_2Sn$ ($M - C_4H_9$)$^+$ m/z 437.1503, found m/z 437.1513.

***O*-Phenyl 2-(Benzoyloxy)hept-3-enethioate (23).** Cross-coupling of **22** with phenyl chlorothionoformate as described in the general procedure gave the title adduct as a colorless oil (65%): TLC (SiO_2) EtOAc/hexane (1:9), R_f ~ 0.38. ^{1}H NMR δ 8.08−8.22 (m, 2H), 7.12−7.60 (m, 6H), 7.00−7.08 (m, 2H), 6.18 (ddt, J = 0.9, 6.8, 14.5 Hz, 1H), 6.10 (d, J = 7.2 Hz, 1H), 5.85 (ddt, J = 1.4, 7.2, 15.4 Hz, 1H), 2.18 (q, J = 7.2 Hz, 2H), 1.42−1.58 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H); ^{13}C NMR δ 216.10, 165.58, 153.95, 137.99, 133.30, 129.90, 129.61, 128.43, 126.58, 124.13, 121.63, 80.91, 34.39, 21.87, 13.60; HRMS (EI) calcd for $C_{20}H_{20}O_3S$ m/z 340.1133, found m/z 340.1140.

***O*-Phenyl 2-Phthalimidononanethioate (24).** Cross-coupling of **13** with phenyl chlorothionoformate as described in the general procedure

(21) Freshly purified organic halides should be used to minimize this rearrangement which is also catalyzed by Bronsted acids: Fichtner, M. W.; Haley, N. F. *J. Org. Chem.* **1981**, *46*, 3141−3143.

(22) Noncatalyzed and Lewis acid-promoted couplings of organostannanes with reactive electrophiles such as allyl halides and acid chlorides are well-known. See ref 1b, Chapter 10.

(23) Ho, T.-L. *Chem. Rev.* **1975**, *75*, 1−20.

(24) A copper-promoted Michael-type addition of alkenyltributylstannanes has been reported: Tanaka, H.; Kameyama, Y.; Sumida, S.-i.; Torii, S. *Tetrahedron Lett.* **1992**, *33*, 7029−7030.

(25) Bhatt, R. K.; Chauhan, K.; Wheelan, P.; Murphy, R. C.; Falck, J. R. *J. Am. Chem. Soc.* **1994**, *116*, 5050−5056.

(26) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543−2549.

(27) Bhatt, R. K.; Ye, J.; Falck, J. R. *Tetrahedron Lett.* **1994**, *35*, 4081−4084.

(28) Bachi, M. D.; Bosch, E.; Denenmark, D.; Girsh, D. *J. Org. Chem.* **1992**, *57*, 6803−6810.

(29) Racherla, U. S.; Brown, H. C. *J. Org. Chem.*, **1991**, *56*, 401−404.

gave the title adduct as a colorless oil (92%). TLC (SiO_2) EtOAc/hexane (1:4), $R_f \sim 0.43$; ^{1}H NMR δ 7.83−7.90 (m, 2H), 7.72−7.79 (m, 2H), 7.30−7.41 (m, 2H), 7.21−7.22 (m, 1H), 6.98−7.04 (m, 2H), 5.20 (dd, J = 6.7, 9.1 Hz, 1H), 2.52−2.63 (m, 2H), 1.20−1.43 (m, 10H), 0.92 (t, J = 6.1 Hz, 3H); ^{13}C NMR δ 216.43, 167.93, 154.42, 134.19, 131.90, 129.65, 126.59, 123.57, 121.75, 61.39, 31.74, 30.84, 29.09, 26.97, 26.80, 22.59, 14.08; HRMS (EI) calcd for $C_{23}H_{25}NO_3S$ *m/z* 395.1555, found *m/z* 395.1564.

***S*-Ethyl 2-Phthalimidononanethioate (25).** Cross-coupling of **13** with ethyl chlorothiolformate as described in the general procedure gave the title adduct as a colorless oil (85%): TLC (SiO_2) EtOAc/hexane (1:4), $R_f \sim 0.33$; ^{1}H NMR δ 7.84−7.93 (m, 2H), 7.71−7.82 (m, 2H), 4.91 (dd, J = 5.0, 10.8 Hz, 1H), 2.88 (q, J = 7.4 Hz, 2H), 2.20−2.38 (m, 2H), 1.15−1.38 (m, 13H), 0.82 (t, J = 6.2 Hz, 3H); ^{13}C NMR δ 196.98, 167.72, 134.30, 131.72, 123.66, 59.88, 31.66, 28.97, 28.81, 28.12, 26.26, 23.60, 22.55, 14.33, 14.03; HRMS (EI) calcd for $C_{19}H_{25}NO_3S$ *m/z* 347.1555, found *m/z* 347.1555.

(*S*)-(1-(Benzoyloxy)-2-methylpropyl)tributylstannane (26). A THF solution (1 mL) of (2-methylpropanoyl)tributylstannane[18] (152 mg, 0.42 mmol) was added dropwise during 15 min to a THF solution (10 mL) of R-BINAL-H [prepared from $LiAlH_4$ (47.8 mg, 1.26 mmol), absolute EtOH (58.1 mg, 1.26 mmol), and (*R*)-(+)-1,1′-bi-2-naphthol (335.6 mg, 1.26 mmol)] at −78 °C. After 20 h, the reaction was quenched with 5 mL of saturated NH_4Cl and extracted with ether (40 mL). The organic layer was washed with water (2 × 10 mL) and brine (10 mL), dried, and concentrated. The residue was suspended in hexane (10 mL), and the precipitated binaphthol was removed by filtration. Concentration of the filtrate afforded the crude α-hydroxy stannane, which was immediately converted to the corresponding benzoyl ester using benzoyl chloride (1.5 equiv) and Et_3N (100 μL) in CH_2Cl_2 (2 mL). Standard aqueous workup and chromatographic purification (SiO_2) with 5% EtOAc/hexane yielded the title compound as a colorless oil (104 mg, 53% overall yield): $[\alpha]^{20}_D$ +7.6° (*c* 1.10, $CHCl_3$); the enantioselectivity (84% ee) was determined by ^{1}H NMR analysis of the derived Mosher (*R*)-MTPA ester[26] [(*R*)-(+)-MTPA, DCC/DMAP, CH_2Cl_2, 5 h]; ^{1}H NMR δ 7.96−8.04 (m, 2H), 7.39−7.58 (m, 3H), 5.92 (d, J = 7.0 Hz, 1H), 2.19−2.37 (m, 1H), 1.38−1.55 (m, 6H), 1.18−1.30 (m, 6H), 1.03 (d, J = 6.6 Hz, 3H), 1.02 (d, J = 6.6 Hz, 3H), 0.80−0.91 (m, 15H); ^{13}C NMR δ 166.63, 132.47, 130.84, 129.30, 128.27, 78.98, 32.32, 29.08, 27.45, 20.77, 20.32, 13.62, 9.94; HRMS (CI, CH_4) calcd for $C_{23}H_{40}O_2Sn$ *m/z* 468.2050, found *m/z* 468.2058.

***S*-Ethyl (*R*)-2-(Benzoyloxy)-3-methylthiobutyrate (27).** Chiral stannane **26** (40 mg, 0.085 mmol) and CuCN (0.6 mg, 0.007 mmol) were suspended in 2 mL of anhydrous toluene. To this was added ethyl chlorothiolformate (9.7 mg, 0.078 mmol), and the whole was heated at 80 °C under an argon atmosphere in a sealed tube for 68 h. Concentration *in vacuo* and chromatographic purification (SiO_2) using 10% EtOAc/hexane gave the title compound (15 mg, 73% yield) as a colorless oil: $[\alpha]^{20}_D$ −18.9° (*c* 0.4, $CHCl_3$); TLC (SiO_2) EtOAc/hexane (1:9), $R_f \sim 0.42$; ^{1}H NMR δ 8.12−8.19 (m, 2H), 7.55−7.62 (m, 1H), 7.42−7.50 (m, 2H), 5.39 (d, J = 4.1 Hz, 1H), 2.91 (q, J = 7.3 Hz, 2H), 2.40−2.51 (m, 1H), 1.23 (t, J = 7.3 Hz, 3H), 1.03 (d, J = 6.8 Hz, 3H), 1.02 (d, J = 6.9 Hz, 3H); ^{13}C NMR δ 199.15, 165.66, 133.47, 129.98, 129.44, 128.56, 82.60, 31.34, 22.81, 18.97, 16.77, 14.47; HRMS (EI) calcd for $C_{14}H_{18}O_3S$ *m/z* 266.0977, found *m/z* 266.0982. The stereochemical purity of the product (83% ee) was determined by chiral HPLC analysis as described below.

Standard of *S*-Ethyl (S)-2-(Benzoyloxy)-3-methylthiobutyrate (ent-27). To a −20 °C CH_2Cl_2 solution (2 mL) of L-α-hydroxyisovaleric acid (118 mg, 1 mmol; Fluka), Et_3N (202 mg, 2 mmol), and DMAP (59 mg, 0.5 mmol) was added benzoyl chloride (182 mg, 1.3 mmol). The mixture was stirred at −20 °C for 1 h, then at room temperature for 12 h. After being diluted with CH_2Cl_2 (10 mL), the reaction mixture was extracted with saturated $NaHCO_3$ (3 × 8 mL). The combined bicarbonate extracts were acidified with cold 1 N HCl and extracted with EtOAc (3 × 8 mL). The organic extracts were washed with water (2 × 5 mL) and dried, and the solvent was removed *in vacuo* to yield a low-melting white solid (133 mg, 60% yield). This was immediately dissolved in CH_2Cl_2 (1 mL) and cooled to 0 °C, and ethyl chloroformate (78 mg, 0.78 mmol) and triethylamine (145 mg, 1.44 mmol) were added. After 10 min, ethanethiol (86 mg, 1.38 mmol) and DMAP (8 mg, 0.06 mmol) were added. Following another 15 min, the mixture was diluted with CH_2Cl_2 (10 mL), washed with cold, saturated $NaHCO_3$ solution (5 mL), and water (2 × 5 mL), and dried. Concentration *in vacuo* and chromatographic purification (SiO_2) of the residue using 10% EtOAc/hexane gave the title compound (67 mg, 42% yield) as a colorless oil: $[\alpha]^{20}_D$ +18.9° (*c* 0.94, $CHCl_3$); spectrally identical with the above (*R*)-isomer **27**. The stereochemical purity (82% ee) was determined by chiral HPLC analysis as described below.

Chiral HPLC Analysis. Isocratic, normal phase HPLC analysis of *S*-ethyl 2-(benzoyloxy)-3-methylthiobutyrate was conducted on a Chiralcel OD column (Daicel Chemical Ind.) (25 × 0.46 cm) using hexane/2-propanol (99.6/0.4 v/v) at a flow rate of 1 mL/min with UV monitoring at 254 nm. Racemic material showed two components of equal size with base line resolution: $R_t \sim 6$ and 7 min for the *R*- and *S*-enantiomers, respectively.

(*S*)-(1-((Pyrrolidinethiocarbamoyl)oxy)decyl)tributylstannane (28). A THF solution (1.5 mL) of decanoyltributylstannane[18] (373 mg, 0.83 mmol) was added dropwise during 20 min to a −78 °C THF solution (12 mL) of R-BINAL-H [prepared from $LiAlH_4$ (95 mg, 2.5 mmol), absolute EtOH (115 mg, 2.5 mmol), and (*R*)-(+)-1,1′-bi-2-naphthol (717 mg, 2.5 mmol). After 2 h, the reaction was quenched with 6 mL of saturated NH_4Cl and the mixture was diluted with ether (60 mL). The organic layer was washed with water (2 × 15 mL) and brine (15 mL), dried, and concentrated *in vacuo*. The residue was suspended in hexane (12 mL), and the precipitated binaphthol was removed by filtration. Concentration of the filtrate afforded the crude α-hydroxy stannane which was immediately converted to the corresponding pyrrolidinecarbamate using thiocarbonyldiimidazole (222 mg, 1.25 mmol) and DMAP (8 mg) in CH_2Cl_2 (2 mL), followed by pyrrolidine (2 mL) as described for **42**.[28] Extractive isolation and chromatographic purification (SiO_2) using EtOAc/hexane (3:97) yielded the title compound (323 mg, 69% yield) as a colorless oil; $[\alpha]^{20}_D$ +40.1° (*c* 1.67, $CHCl_3$); its stereochemical purity (96% ee) was determined by ^{1}H NMR analysis of the derived Mosher (*R*)-MTPA ester[26] [(*R*)-(+)-MTPA, DCC/DMAP, CH_2Cl_2, 5 h]; ^{1}H NMR δ 5.58 (dd, J = 4.9, 8.9 Hz, 1H), 3.64−3.78 (m, 2H), 3.36−3.50 (m, 2H), 1.80−2.00 (m, 4H), 1.38−1.60 (m, 8H), 1.08−1.37 (m, 20H), 0.80−1.00 (m, 18H); ^{13}C NMR δ 185.34, 79.35, 51.80, 47.49, 34.70, 31.86, 29.51, 29.48, 29.25, 29.13, 28.97, 28.94, 27.49, 25.72, 24.62, 22.66, 14.09, 13.69, 10.10; MS (CI, CH_4) *m/z* (relative intensity) 560 (M^+, 6), 504 (100), 502 (80), 364 (42), 362 (36), 291 (20), 177 (22), 114 (46) 98 (41), 55 (36); HRMS (EI) calcd for $C_{23}H_{46}NOSSn$ ($M - C_4H_9$)$^+$ *m/z* 504.2322, found *m/z* 504.2318.

4(*R*)-((Pyrrolidinethiocarbamoyl)oxy)tridec-1-ene (29). Allyl bromide (14 mg, 0.12 mmol) was added to **28** (72 mg, 0.13 mmol) and copper cyanide (0.9 mg, 0.01 mmol) in 1.5 mL of anhydrous THF. The reaction mixture was heated at 45 °C under an argon atmosphere in a sealed tube for 14 h. Concentration *in vacuo* and chromatographic purification (SiO_2) using 5% EtOAc/hexane gave the title compound (34 mg, 94.5% yield) as a colorless oil: $[\alpha]^{20}_D$ +8.8° (*c* 1.08, $CHCl_3$); ^{1}H NMR δ 5.70−5.82 (m, 1H), 5.40−5.50 (m, 1H), 5.00−5.10 (m, 2H), 3.70 (t, 6.1 Hz, 2H), 3.50 (t, J = 6.9 Hz, 2H), 2.41 (t, J = 5.9 Hz, 2H), 1.82−2.00 (m, 4H), 1.54−1.76 (m, 2H), 1.13 (br s, 14H), 0.83 (t, J = 6.4 Hz, 3H); ^{13}C NMR: δ 184.81, 133.88, 117.47, 79.85, 51.83, 47.62, 38.24, 33.26, 31.89, 29.56, 29.52, 29.50, 29.29, 25.55, 25.07, 24.52, 22.67, 14.09; MS (CI, CH_4) *m/z* (relative intensity) 311 (M^+, 4), 279 (2), 160 (10), 132 (100), 97 (17), 55 (13); HRMS (EI) calcd for $C_{18}H_{33}NOS$ *m/z* 311.2283, found *m/z* 311.2279. This product's absolute stereochemistry and % ee were determined after hydrolysis by comparisons with an authentic standard of (4*R*)-tridec-1-en-4-ol and the corresponding Mosher esters (*vide infra*).

Standard of (4*R*)-Tridec-1-en-4-ol. A hexane solution (1 M) of DIBAL-H (30.2 mg, 0.21 mmol) was added dropwise during 15 min to the above thiocarbamate (22 mg, 0.07 mmol) in anhydrous hexane (1 mL) at −45 °C. After 1h at −45 °C, the reaction mixture was slowly warmed to 0 °C and stirred another 3 h. The reaction was quenched with saturated NH_4Cl (1 mL) and extracted with ether (3 × 10 mL), and the combined ethereal extracts were washed with saturated potassium sodium tartrate (2 × 10 mL), water (10 mL), and brine (10 mL), dried, and concentracted *in vacuo* to yield the title compound (13.5 mg, 97%) as a colorless oil: $R_f \sim 0.40$ (1:5) EtOAc/hexane; spectrally identical with an authentic sample;[30] $[\alpha]^{20}_D$ +7.3° (*c* 1.15, $CHCl_3$) (lit.[30] for (4*S*)-isomer, $[\alpha]^{23}_D$ −10.4° (*c* 6.7, C_6H_6)). The

(30) Riediker, M.; Duthaler, R. F. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 494−495.

stereochemical purity (96% ee) was determined by ^{1}H NMR analysis of the derived Mosher (*R*)-MTPA ester[26] [(*R*)-(+)-MTPA, DCC/DMAP, CH_2Cl_2, 4 h].

(1-((*N*,*N*-Dimethylthiocarbamoyl)oxy)octyl)tributylstannane (30). The title compound was obtained[6a] from *n*-octanal and dimethylthiocarbamoyl chloride as a colorless oil (54%) after chromatography using EtOAc/hexane (3:97): ^{1}H NMR δ 5.54 (dd, J = 4.9, 9.2 Hz, 1H), 3.38 (s, 3H), 3.02 (s, 3H), 1.78−1.94 (m, 2H), 1.38−1.60 (m, 6H), 1.09−1.37 (m, 16H), 0.80−1.00 (m, 18H); ^{13}C NMR δ 188.17, 80.26, 42.49, 37.33, 34.60, 31.75, 29.36, 29.16, 29.07, 27.49, 27.42, 22.58, 14.03, 13.63, 10.09; MS (CI, CH_4) *m/z* (relative intensity) 506 (M^+, 8), 450 (100), 448 (78), 338 (40), 291(20), 224 (12), 177 (16), 88 (50), 72 (36); HRMS (EI) calcd for $C_{19}H_{40}NOSSn$ ($M - C_4H_9)^+$ *m/z* 450.1855, found *m/z* 450.1848.

8-((*N*,*N*-Dimethylthiocarbamoyl)oxy)octadec-10-yne (31). Cross-coupling of **30** with 1-bromo-2-decyne as described in the general procedure gave the title adduct as a colorless oil (84%): TLC (SiO_2) EtOAc/hexane (1:9), $R_f \sim 0.39$; ^{1}H NMR δ 5.49−5.04 (m, 1H), 3.37 (s, 3H), 3.05 (s, 3H), 2.48−2.59 (m, 2H), 2.03−2.18 (m, 2H), 1.67−1.84 (m, 2H), 1.15−1.42 (m, 20H), 0.82−0.98 (m, 6H); ^{13}C NMR δ 187.58, 82.40, 79.31, 75.26, 42.55, 37.65, 32.68, 31.79, 29.47, 29.15, 28.99, 28.84, 28.79, 25.11, 23.88, 22.64, 18.73, 14.08; MS (CI, CH_4) *m/z* (relative intensity) 353 (M^+, 58), 320 (7), 281 (19), 243 (30), 106 (100), 72 (34); HRMS (EI) calcd for $C_{21}H_{39}NOS$ *m/z* 353.2752, found *m/z* 353.2739.

6-((*N*,*N*-Dimethylthiocarbamoyl)oxy)trideca-5-one (32). Cross-coupling of **30** with pentanoyl chloride as described in the general procedure gave the title adduct as a colorless oil (82%): TLC (SiO_2) EtOAc/hexane (3:17), $R_f \sim 0.39$; ^{1}H NMR δ 5.62 (t, J = 6.3 Hz, 1H), 3.40 (s, 3H), 3.22 (s, 3H), 2.40−2.60 (m, 2H), 1.50−1.82 (m, 4H), 1.10−1.40 (m, 14H), 0.85−0.96 (m, 6H); ^{13}C NMR δ 208.08, 187.59, 84.32, 42.93, 38.59, 37.97, 31.69, 30.91, 29.25, 29.01, 25.38, 25.20, 22.59, 22.31, 14.05, 13.88; MS (CI, CH_4) *m/z* (relative intensity) 301 (M^+, 100), 256 (7), 216 (6), 144 (7), 88 (10), 72 (57); HRMS (EI) calcd for $C_{16}H_{31}NO_2S$ *m/z* 301.2076, found *m/z* 301.2082.

***O*-Phenyl *O*-(1-(Tributylstannyl)-3-phenylpropyl) Thiocarbonate (33).** The title compound was obtained[6a] from dihydrocinnamaldehyde and phenyl chlorothionoformate as a colorless oil (69%) after chromatography using EtOAc/hexane (3:97): ^{1}H NMR δ 7.36−7.48 (m, 2H), 7.12−7.30 (m, 6H), 7.06−7.10 (m, 2H), 5.42 (dd, J = 4.1, 10.1 Hz, 1H), 2.72−2.88 (m, 1H), 2.60−2.71 (m, 1H), 2.34−2.50 (m, 1H), 2.02−2.20 (m, 1H), 1.40−1.62 (m, 6H), 1.23−1.40 (m, 6H), 0.80−1.03 (m, 15H); ^{13}C NMR δ 193.90, 153.56, 141.39, 129.54, 128.54, 126.45, 126.07, 122.06, 83.38, 36.38, 34.26, 29.09, 27.54, 13.78, 10.42; MS (CI, CH_4) *m/z* (relative intensity) 561 (M^+, 2), 505 (70), 503 (57). 327 (43), 91 (64), 77 (43); HRMS (EI) calcd for $C_{24}H_{33}O_2SSn$ ($M-C_4H_9)^+$ *m/z* 505.1223, found *m/z* 505.1228.

***O*-Phenyl *O*-(1-Phenylhex-5-en-3-yl) Thiocarbonate (34).** Cross-coupling of **33** with allyl bromide as described in the general procedure gave the title adduct as a colorless oil (23%): TLC (SiO_2) EtOAc/hexane (1:9) $R_f \sim 0.62$; ^{1}H NMR δ 7.50−7.03 (m, 10H), 5.72−5.83 (m, 1H), 5.32−5.43 (m, 1H), 5.08−5.14 (m, 2H), 2.63−2.80 (m, 1H), 5.08−5.14 (m, 2H), 2.63−2.80 (m, 2H), 2.55 (t, J = 6.7 Hz, 2H), 1.93−2.12 (m, 2H); ^{13}C NMR δ 194.63, 153.31, 141.12, 132.59, 129.48, 128.38, 126.49, 126.08, 121.99, 118.63, 83.98, 37.76, 34.77, 31.54; HRMS (EI) calcd for $C_{19}H_{20}O_2S$ *m/z* 312.1184, found *m/z* 312.1179.

***O*-Phenyl *S*-(1-Phenylhex-5-en-3-yl) Thiocarbonate (35).** Cross-coupling of **33** with allyl bromide as described in the general procedure gave the title adduct as a colorless oil (48%): TLC (SiO_2) EtOAc/hexane (1:9), $R_f \sim 0.58$; ^{1}H NMR δ 7.08−7.42 (m, 10H), 5.70−5.88 (m, 1H), 5.03−5.18 (m, 2H), 3.42−3.56 (m, 1H), 2.63−2.84 (m, 2H), 2.54 (t, J = 6.9 Hz, 2H), 1.83−2.06 (m, 2H); ^{13}C NMR δ 169.83, 151.18, 141.26, 134.38, 129.49, 128.48, 128.40, 126.11, 126.06, 121.34, 118.10, 46.39, 39.36, 35.66, 33.56; HRMS (EI) calcd for $C_{19}H_{20}O_2S$ *m/z* 312.1184, found *m/z* 312.1192.

(1-((*N*,*N*-Dimethylthiocarbamoyl)oxy)-3-phenylpropyl)tributylstannane (36). The title compound was obtained[6a] from dihydrocinnamaldehyde and dimethylthiocarbamoyl chloride as a colorless oil (57%) after chromatography using EtOAc/hexane (3:97): ^{1}H NMR δ 7.10−7.30 (m, 5H), 5.58 (dd, J = 4.8, 9.3 Hz, 1H), 3.37 (s, 3H), 3.03 (s, 3H), 2.59−2.84 (m, 2H), 2.21−2.38 (m, 1H), 2.02−2.20 (m, 1H), 1.40−1.58 (m, 6H), 1.21-1.39 (m, 6H), 0.90−1.03 (m, 15H); ^{13}C NMR: δ 188.05, 141.96, 128.37, 128.35, 125.82, 79.84, 42.64, 37.40, 36.79, 34.36, 29.13, 27.49, 13.72, 10.28; MS (CI, CH_4) *m/z* (relative intensity) 512 (M^+, 6), 456 (100), 338 (35), 291 (23), 289 (17), 177 (14), 88 (37), 72 (43); HRMS (EI) calcd for $C_{20}H_{34}NOSSn$ ($M - C_4H_9)^+$ *m/z* 456.1383, found *m/z* 456.1388.

1-Phenyl-3-((*N*,*N*-dimethylthiocarbamoyl)oxy)-6-methyl-5-heptene (37). Cross-coupling of **36** with prenyl bromide as described in the general procedure gave the title adduct as a colorless oil (50%): TLC (SiO_2) EtOAc/hexane (3:17), $R_f \sim 0.40$. ^{1}H NMR δ 7.16−7.38 (m, 5H), 5.50−5.60 (m, 1H), 5.10 (t, J = 7.4 Hz, 1H), 3.38 (s, 3H), 3.02 (s, 3H) 2.50−2.78 (m, 2H), 2.35−2.45 (m, 2H), 1.90−2.00 (m, 2H), 1.70 (s, 3H), 1.61 (s, 3H); ^{13}C NMR δ 187.76, 144.34, 141.94, 128.28, 128.20, 125.78, 118.74, 81.26, 42.55, 41.69. 37.49, 35.02, 31.85, 25.86, 23.62; MS (CI, CH_4): *m/z* (relative intensity) 290 [($M - H)^+$, 10], 258 (7), 186 (59), 131 (39), 106 (100), 95 (72); HRMS (EI) calcd for $C_{17}H_{25}NOS$ *m/z* 291.1657, found *m/z* 291.1650.

1-Phenyl-3-((*N*,*N*-dimethylthiocarbamoyl)oxy)-4,4-dimethyl-5-hexene (38). Cross-coupling of **36** with prenyl bromide as described in the general procedure gave the title adduct as a colorless oil (42%): TLC (SiO_2) EtOAc/hexane (3:17), $R_f \sim 0.40$; ^{1}H NMR δ 7.16−7.38 (m, 5H), 5.90 (dd, J = 11.4, 16.8 Hz, 1H), 5.68 (dd, J = 2.9, 9.6 Hz, 1H), 4.98−5.06 (m, 2H), 3.43 (s, 3H), 3.10 (s, 3H), 2.50−2.78 (m, 2H), 2.35−2.45 (m, 2H), 1.90−2.00 (m, 2H), 1.01 (s, 6H); ^{13}C NMR δ 189.00, 142.38, 134.47, 128.75, 128.27, 125.68, 112.69, 86.92, 42.86, 37.57, 32.86, 32.75, 32.47, 23.62, 18.03; MS (CI, CH_4) *m/z* (relative intensity) 290 [($M - H)^+$, 10], 258 (7), 186 (59), 131 (39), 106 (100), 95 (72); HRMS (EI) calcd for $C_{17}H_{25}NOS$ *m/z* 291.1657, found *m/z* 291.1650.

(1-(Thionoacetyloxy)-3-phenylpropyl)tributylstannane (39). A mixture of **8** (120 mg, 0.26 mmol) and Lawesson's reagent (421 mg, 1.04 mmol) was suspended in dry toluene (2 mL) and heated under argon at 115 °C. After 4 h, the mixture was cooled, filtered through Celite, and concentrated. The residue yielded the title compound (32 mg, 26%) as a colorless oil after chromatography: TLC (SiO_2) EtOAc/hexane (1:9), $R_f \sim 0.64$; ^{1}H NMR δ 7.10−7.28 (m, 5H), 5.42 (dd, J = 3.9, 10.40 Hz, 1H), 2.62−2.79 (m, 1H), 2.52−2.60 (m, 1H), 2.50 (s, 3H), 2.30−2.40 (m, 1H), 1.82−2.04 (m, 1H), 1.30−1.44 (m, 6H), 1.18−1.25 (m, 6H), 0.75−0.97 (m, 15H); ^{13}C NMR δ 217.35, 141.47, 128.43, 128.39, 125.90, 81.75, 36.11, 34.38, 34.03, 29.01, 27.40, 13.66, 10.35; MS (CI, CH_4) *m/z* (relative intensity) 483 (M^+, 2), 427 (100), 425 (80), 309 (40), 291 (79), 289 (58), 235 (22), 177 (21), 91 (40), 59 (26); HRMS (EI) calcd for $C_{19}H_{31}OSSn$ ($M-C_4H_9)^+$ *m/z* 427.1118, found *m/z* 427.1123.

1-Phenyl-3-(thionoacetyloxy)-6-methyl-5-heptene (40). Cross-coupling of **39** with prenyl bromide as described in the general procedure gave the title adduct as a colorless oil (61%): TLC (SiO_2) EtOAc/hexane (5:95), $R_f \sim 0.58$; ^{1}H NMR δ 7.18−7.38 (m, 5H), 5.47−5.60 (m, 1H), 5.04−5.10 (m, 1H), 2.60−2.80 (m, 2H), 2.46 (s, 3H), 2.30−2.40 (m, 2H), 1.88−2.03 (m, 2H), 1.70 (s, 3H), 1.61 (s, 3H); ^{13}C NMR δ 219.68, 141.51, 135.02, 128.40, 128.34, 125.93, 118.32, 81.93, 35.00, 34.62, 32.72, 31.80, 25.84, 17.94; MS (CI, CH_4) *m/z* (relative intensity) 262 (M^+, 1), 229 (2), 186 (67), 131 (72), 95 (100), 69 (52); HRMS (EI) calcd for $C_{16}H_{22}OS$ *m/z* 262.1391, found *m/z* 262.1395.

1-Phenyl-3-(thionoacetyloxy)-4,4-dimethyl-5-hexene (41). Cross-coupling of **39** with prenyl bromide as described in the general procedure gave the title adduct as a colorless oil (17%): TLC (SiO_2) EtOAc/hexane (5:95), $R_f \sim 0.58$; ^{1}H NMR δ 7.18−7.38 (m, 5H), 5.72−5.87 (m, 2H), 4.97−5.03 (m, 2H), 2.60−2.80 (m, 2H), 2.59 (s, 3H), 1.84−1.98 (m, 2H), 1.02 (s, 6H); ^{13}C NMR δ 219.68, 143.88, 141.81, 135.02, 128.40, 128.33, 113.07, 41.76, 35.00, 32.72, 32.51, 23.14, 22.79, 17.97; MS (CI, CH_4): 262 (M^+, 1); HRMS (EI) calcd for $C_{16}H_{22}OS$ *m/z* 262.1391, found *m/z* 262.1389.

(α-((Pyrrolidinethiocarbamoyl)oxy)benzyl)tributylstannane (42). To a solution of benzaldehyde (318 mg, 3 mmol) and $Bu_3SnSiMe_3$ (1.63 g, 4.5 mmol) in benzene (6 mL) at 10 °C was added a solution of Bu_4NCN (25 mg, 0.09 mmol) in benzene (1 mL) as previously described.[27] After 0.6 h, the reaction mixture was quenched with saturated NH_4Cl solution (6 mL) and extracted with Et_2O (2 × 6 mL). The combined ethereal extracts were washed with 1 N HCl solution (2 × 5 mL), H_2O (2 × 5 mL), and brine (6 mL) and concentrated *in vacuo* to give the corresponding (α-hydroxybenzyl)tributylstannane (>95% crude) as a colorless oil. Without purification, the adduct was dissolved in CH_2Cl_2 (5 mL) containing DMAP (10 mg) and thiocar-

bonyldiimidazole[28] (0.80 g, 4.5 mmol). After 30 min, the reaction mixture was filtered through a short bed of silica gel and the product was eluted with 10% EtOAc/hexane (100 mL) to give a labile (α-((imidazolethiocarbamoyl)oxy)benzyl)tributylstannane that was used immediately in the next reaction without further characterization.

The imidazole in the above carbamate was exchanged by stirring in neat pyrrolidine (3 mL) for 30 min.[28] The excess pyrrolidine was evaporated *in vacuo*, and the residue was flash chromatographed using EtOAc/hexane (3:97) to give **42** (73% overall) as a colorless oil: ^{1}H NMR δ 7.24−7.30 (m, 2H), 7.03−7.10 (m, 3H), 6.62 (s, 1H), 3.61−3.72 (m, 4H), 1.85−2.00 (m, 4.H), 1.30−1.41 (m, 6H), 1.18−1.29 (m, 6H), 0.78−0.94 (m, 15H); ^{13}C NMR δ 184.88, 143.14, 128.26, 124.72, 123.47, 79.79, 51.94, 47.70, 28.74, 27.72, 25.69, 24.49, 13.53, 10.36; MS (CI, CH_4) *m/z* (relative intensity) 510 (M^+, 6), 454 (100), 364 (43), 362 (36), 176 (17), 114 (15), 98 (55), 55 (38); HRMS (EI) calcd for $C_{20}H_{32}NOSn$ $(M - C_4H_9)^+$ *m/z* 454.1227, found *m/z* 454.1245.

***S*-Ethyl 2-((Pyrrolidinethiocarbamoyl)oxy)-2-phenylthioacetate (43).** Cross-coupling of **42** with ethyl chlorothioformate as described in the general procedure gave the title adduct as a colorless oil (77%): TLC (SiO_2) EtOAc/hexane (3:17), $R_f \sim 0.30$; ^{1}H NMR δ 7.42−7.60 (m, 2H), 7.37−7.41 (m, 3H), 6.90 (s, 1H), 3.60−4.00 (m, 4H), 2.89 (q, $J = 7.4$ Hz, 2H), 1.87−2.20 (m, 4H), 1.12 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR δ 197.57, 183.17, 135.05, 128.96, 128.66, 127.61, 84.75, 52.41, 48.43, 25.69, 24.54, 23.08, 14.25; MS (CI, CH_4) *m/z* (relative intensity) 309 (M^+, 6), 248 (71), 151 (100), 114 (64), 98 (51); HRMS (CI) calcd for $C_{15}H_{19}NO_2S_2$ *m/z* 309.0857, found *m/z* 309.0855.

1-((Pyrrolidinethiocarbamoyl)oxy)-1-phenyl-3-butene (44). Cross-coupling of **42** with allyl bromide as described in the general procedure gave the title adduct as a colorless oil (99%): TLC (SiO_2) EtOAc/hexane (3:17), $R_f \sim 0.44$; ^{1}H NMR δ 7.23−7.39 (m, 5H), 6.48 (t, $J =$ 4.8 Hz, 1H), 5.63−5.81 (m, 1H), 5.00−5.15 (m, 2H), 3.50−3.80 (m, 4H), 2.57−2.80 (m, 2H), 1.82−2.00 (m, 4H); ^{13}C NMR δ 184.19, 140.21, 133.29, 128.26, 127.66, 126.66, 117.92, 80.72, 51.94, 47.80, 41.00, 25.56, 24.46; MS (CI, CH_4) *m/z* (relative intensity) 261 (M^+, 8), 229 (5), 160 (8), 130 (100), 98 (18), 91 (12), 55 (10); HRMS (EI) calcd for $C_{15}H_{19}NOS$ *m/z* 261.1187, found *m/z* 261.1197.

***O*-Phenyl *S*-(1-(Tributylstannyl)-3-phenylpropyl) Thiocarbonate (46).** The title compound was obtained as a colorless oil from the copper- or trifluoroacetic acid-catalyzed[21] rearrangement of **33** at room temperature for 6 h: TLC (SiO_2) EtOAc/hexane (5:95), $R_f \sim 0.50$; ^{1}H NMR δ 7.10−7.42 (m, 10H), 2.84 (t, $J = 6.6$ Hz, 1H), 2.70−2.80 (m, 2H), 2.10−2.20 (m, 2H), 1.42−1.61 (m, 6H), 1.24−1.38 (m, 6H), 0.83−1.05 (m, 15H); ^{13}C NMR δ 172.37, 151.37, 141.57, 129.45, 128.42, 128.39, 125.96, 125.91, 121.34, 36.67, 35.68, 29.03, 27.40, 26.74, 13.68, 10.23; HRMS (EI) calcd for $C_{24}H_{33}O_2SSn$ $(M - C_4H_9)^+$ *m/z* 505.1223, found *m/z* 505.1231.

***O*-(1-(Tributylstannyl)-3-phenylpropyl) *S*-Ethyl Thiocarbonate (47).** The title compound was obtained[6a] from dihydrocinnamaldehyde and ethyl chlorothioformate as a colorless oil (72%): TLC (SiO_2) EtOAc/hexane (1:9), $R_f \sim 0.58$. ^{1}H NMR δ 7.16−7.38 (m, 5H), 4.97 (dd, $J = 4.0$, 9.8 Hz, 1H), 3.86 (q, $J = 7.4$ Hz, 2H), 2.72−2.80 (m, 1H), 2.52−2.64 (m, 1H), 2.18−2.30 (m, 1H), 1.90−2.22 (m, 1H), 1.38−1.57 (m, 6H), 1.20−1.32 (m, 9H), 0.74−1.00 (m, 15H); ^{13}C NMR δ 170.93, 141.48, 128.44, 128.37, 125.86, 75.00, 36.28, 33.99, 28.81, 27.40, 25.30, 15.23, 13.65, 9.56; HRMS (EI) calcd for $C_{20}H_{33}O_2SSn$ $(M - C_4H_9)^+$ *m/z* 457.1223, found *m/z* 457.1230.

(1-(Methylthiomethoxy)-3-phenylpropyl)tributylstannane (48). The title compound was obtained[6a] from dihydrocinnamaldehyde and chloromethyl methyl sulfide as a colorless oil (51%): TLC (SiO_2) 10% EtOAc/hexane, $R_f \sim 0.53$; ^{1}H NMR δ 7.12−7.34 (m, 5H), 4.70 (d, J = 11.3 Hz, 1H), 4.49 (d, $J = 11.3$ Hz, 1H), 4.21 (dd, $J = 5.3$, 7.8 Hz, 1H), 2.60−2.80 (m, 2H), 2.20 (s, 3H), 1.96−2.18 (m, 2H), 1.40−1.58 (m, 6H), 1.12−1.38 (m, 6H), 0.80−1.00 (m, 15H); ^{13}C NMR δ 142.35, 128.34, 128.30, 125.73, 74.98, 73.66, 36.85, 34.50, 29.22, 27.49, 14.22, 13.68, 9.31; HRMS (EI) calcd for $C_{19}H_{33}OSSn$ $(M - C_4H_9)^+$ *m/z* 429.1274, found *m/z* 429.1269.

(1-((2-Thiophenecarbonyl)oxy)-3-phenylpropyl)tributylstannane (49). The title compound was obtained[6a] from dihydrocinnamaldehyde and 2-thiophenecarbonyl chloride (Aldrich Chemical Co.) as a colorless oil (84%): TLC (SiO_2) 10% EtOAc/hexane, $R_f \sim 0.67$; ^{1}H NMR δ 0.82−0.98 (m, 15H), 1.20−1.36 (m, 6H), 1.41−1.58 (m,6H), 2.05−2.37 (m, 1H), 2.31−2.42 (m, 1H), 2.61−2.85 (m, 2H), 5.02 (dd, $J = 6.1$, 8.0 Hz, 1H), 7.06−7.35 (m, 6H), 7.55 (d, $J = 4.2$ Hz, 1H), 7.78 (d, $J = 4.2$ Hz, 1H); ^{13}C NMR δ 9.67, 13.67, 27.40, 29.03, 34.18, 36.20, 71.83, 125.84, 127.64, 128.39, 128.45, 131.81, 132.72, 141.64, 162.59; HRMS (EI) calcd for $C_{22}H_{31}O_2SSn$ $(M - C_4H_9)^+$ *m/z* 479.1067, found *m/z* 479.1073.

1-Phenyl-3-((2-thiophenecarbonyl)oxy)hex-5-ene (50). Cross-coupling of **49** with allyl bromide as described in the general procedure gave the title adduct as a colorless oil (50%): TLC (SiO_2) 10% EtOAc/hexane, $R_f \sim 0.50$; ^{1}H NMR δ 1.95−2.18 (m, 2H), 2.45 (t, $J = 7.2$ Hz, 2H), 2.62−2.81 (m, 2H), 5.05−5.21 (m, 3H), 5.74−5.90 (m, 2H), 7.05−7.31 (m, 5H), 7.58 (d, $J = 4.2$ Hz, 1H), 7.82 (d, $J = 4.2$ Hz, 1H); ^{13}C NMR δ 31.71, 35.39, 38.70, 73.86, 118.13, 125.94, 127.72, 128.34, 128.43, 132.23, 133.26, 134.18, 141.45, 161.89; HRMS (EI) calcd for $C_{17}H_{18}O_2S$ *m/z* 286.1028, found *m/z* 286.10224.

(1-((Diphenylphosphinyl)oxy)-3-phenylpropyl)tributylstannane (51). The title compound was obtained[6a] from dihydrocinnamaldehyde and diphenylphosphinic chloride (Aldrich Chemical Co.) as a colorless oil (71%): TLC (SiO_2) 20% EtOAc/hexane, $R_f \sim 0.30$; ^{1}H NMR δ 0.81−1.03 (m, 15H), 1.24−1.38 (m, 6H), 2.12−2.20 (m, 2H), 2.60−2.74 (m, 2H), 4.58−4.78 (m, 1H), 7.05−7.25 (m, 5H), 7.41−7.51 (m, 6H), 7.72−7.85 (m, 4H); HRMS (EI) calcd for $C_{35}H_{38}O_2PSn$ $(M - C_4H_9)^+$ *m/z* 641.1634, found *m/z* 641.1631.

1-Phenyl-3-((diphenylphosphinyl)oxy)hex-5-ene (52). Cross-coupling of **51** with allyl bromide as described in the general procedure gave the title adduct as a colorless oil (66%): TLC (SiO_2) EtOAc/hexane (1:4), $R_f \sim 0.05$; ^{1}H NMR δ 1.95−2.01 (m, 2H), 2.50 (t, $J =$ 7.2 Hz, 2H), 2.57−2.71 (m, 2H), 4.51−4.60 (m, 1H), 5.02−5.10 (m, 2H), 5.73−5.82 (m, 1H), 7.02−7.23 (m, 5H), 7.41−7.58 (m, 6H). 7.78−7.90 (m, 4H); ^{13}C NMR δ 31.18, 36.43, 39.85, 75.57, 118.24, 125.85, 128.29, 128.35, 128.49, 131.59, 131.75, 131.99, 133.11, 141.50; HRMS (EI) calcd for $C_{24}H_{25}O_2P$ *m/z* 376.1592, found *m/z* 376.1591.

(1-(Acetyloxy)-3-((pyrrolidinethiocarbamoyl)oxy)propyl)tributylstannane (53). To a mixture of 1,3-propanediol (300 mg, 3.95 mmol) and DMAP (540.4 mg, 4.34 mmol) in CH_2Cl_2 (10 mL) was added Ph_3CBr (1.4 g, 4.34 mmol) in CH_2Cl_2 (10 mL) at 0 °C. After stirring at room temperature for 10 h, the reaction mixture was washed with water (20 mL × 3) and brine, dried, and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2) to give the monotrityl ether (975 mg, 76%). The remaining alcohol (975 mg, 3.06 mmol) was oxidized by stirring with PCC (970 mg, 4.5 mmol) in CH_2Cl_2 (10 mL) for 3 h. The reaction was diluted with ether (10 mL) and passed through a short silica gel column, and the eluent was evaporated to give the corresponding aldehyde (682.5 mg, 70%), sufficiently pure to be used directly in the next step: TLC (SiO_2) 20% EtOAc/hexane, $R_f \sim 0.27$; ^{1}H NMR δ 2.64 (dt, $J = 3.1$, 6.2 Hz, 2H), 3.51 (t, $J = 6.2$ Hz, 2H), 7.21−7.59 (m, 15H), 9.78 (t, $J = 3.1$ Hz, 1H).

By following the procedure[27] used to prepare **42**, the above aldehyde was converted to the related α-(acetyloxy) tributylstannane: TLC (SiO_2) 20% EtOAc/hexane, $R_f \sim 0.60$; ^{1}H NMR δ 0.79−1.05 (m, 15H), 1.20−1.38 (m, 6H), 1.38−1.46 (m, 6H), 1.91 (s, 3H), 1.91−2.20 (m, 2H), 3.10−3.21 (m, 2H), 4.92 (dd, $J = 3.6$, 7.2 Hz, 1H), 7.21−7.29 (m, 10H). 7.29−7.42 (m, 5H). The stannane (949.4 mg, 3.97 mmol) was dissolved in a mixture of formic acid (2 mL) and ether (2 mL). After 15 min, the reaction mixture was diluted with ether (5 mL) and washed with saturated $NaHCO_3$ (5 mL × 3), water, and brine, dried, and concentrated *in vacuo*. The residue was purified by silica gel chromatography to give the detritylated stannane which was dissolved in CH_2Cl_2 (5 mL) containing DMAP (2 mg). To this solution was added thiocarbonyldiimidazole (178.2 mg, 1.0 mmol) in CH_2Cl_2 (2 mL) at 0 °C. After 30 min at room temperature, the reaction mixture was filtered through a short bed of silica gel and washed with 50% EtOAc/hexane (50 mL) and the solvent was evaportated. The residue was dissolved in pyrrolidine (2 mL) and stirred at 23 °C for 30 min. The excess pyrrolidine was evaporated, and the residue was purified by silica gel chromatography (EtOAc/hexane 1:9) to yield **53** (285 mg, 42.7%): TLC (SiO_2) 20% EtOAc/hexane, $R_f \sim 0.41$; ^{1}H NMR δ 0.78−1.02 (m, 15H), 1.21−1.40 (m, 6H), 1.40−1.60 (m, 6H), 1.88−1.92 (m, 4H), 2.03 (s, 3H), 2.03−2.37 (m, 2H), 3.52 (t, $J = 6.6$ Hz, 2H), 3.71 (t, $J = 6.6$ Hz, 2H), 4.41−4.52 (m, 2H), 4.84 (dd, $J = 3.8$, 11.1 Hz, 1H); ^{13}C NMR δ 9.57, 13.68, 20.94, 24.57, 25.67, 27.42, 28.98, 47.76, 51.95, 67.26, 68.16, 171.30, 185.09; HRMS (CI, CH_4) calcd for $C_{18}H_{34}NO_3SSn$ $(M - C_4H_9)^+$ *m/z* 464.1281, found *m/z* 464.1275.

(1-((Pyrrolidinethiocarbamoyl)oxy)-3-phenylpropyl)tributylstannane (54). By following the procedure used to prepare **42**, the title compound was obtained from dihydrocinnamaldehyde, thiocarbonyldiimidazole, and pyrrolidine as a colorless oil (74%) after chromatography with EtOAc/hexane (3:97): ^{1}H NMR δ 7.12−7.38 (m, 5H), 5.60 (dd, J = 3.9, 9.7 Hz, 1H), 3.78 (t, J = 6.9 Hz, 2H), 3.44 (t, J = 6.8 Hz, 2H), 2.60−2.80 (m, 2H), 2.22−2.40 (m, 1H), 2.00−2.18 (m, 1H), 1.82−2.00 (m, 4H), 1.40−1.60 (m, 6H), 1.23−1.38 (m, 6H), 0.80−1.03 (m, 15H); ^{13}C NMR δ 185.13, 142.03, 128.32, 128.29, 125.74, 78.86, 51.84, 47.45, 36.78, 34.32, 29.09, 27.47, 25.71, 24.59, 13.68, 10.19; HRMS (EI) calcd for $C_{22}H_{36}NOSSn$ $(M - C_4H_9)^+$ m/z 482.1540, found m/z 482.1547.

3-(1-((Pyrrolidinethiocarbamoyl)oxy)-3-phenylpropyl)cyclohexanone (55). To a stirring suspension of **54** (32 mg, 0.06 mmol) and CuCN (0.5 mg, 0.006 mmol) in ethylene glycol dimethyl ether (DME) (1 mL) at room temperature under argon was added a DME solution (0.2 mL) of freshly distilled chlorotrimethylsilane (12 mg, 0.11 mmol) and 2-cyclohexen-1-one (5.3 mg, 0.055 mmol). After 7 h at 50 °C, the reaction mixture was diluted with ether (10 mL), washed with 0.5 N HCl (3 mL) and water (10 mL), and dried. Concentration *in vacuo* and chromatographic purification (SiO_2) of the residue using 20% EtOAc/hexane gave the title compound (15 mg, 79%) as a *ca.* 2:1 diastereomeric mixture: ^{1}H NMR δ 7.10−7.35 (m, 5H), 5.57−5.72 (m, 1H), 3.60−3.78 (m, 2H), 3.26−3.50 (m, 2H), 2.67 (br t, J = 7.2 Hz, 2H), 1.90−2.45 (m, 13H), 1.40−1.74 (m, 2H); ^{13}C NMR δ 211.00, 184.89, 141.61, 128.37, 128.26, 125.93, 82.50, 52.18, 47.70, 43.33, 42.24, 41.33, 33.41, 31.64, 27.77, 25.57, 24.98, 24.46; HRMS (EI) calcd for $C_{20}H_{27}NO_2S$ m/z 345.1763, found m/z 345.1760.

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Supplementary Material Available: ^{1}H and/or ^{13}C NMR spectra for all new compounds (84 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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